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Centrotriindane- and triptindane-based polymers of intrinsic microporosity**

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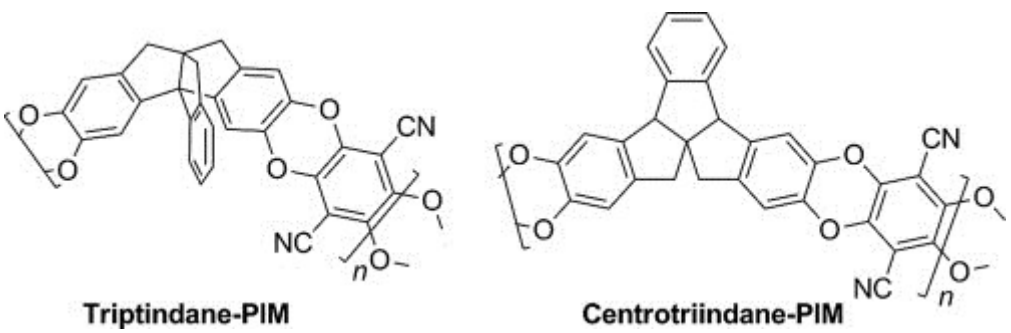
Supporting information:
Supplementary information including, synthetic procedures, physical methodology, crystallographic data and ^{13}C solid state NMR spectra, can be found at http://dx.doi.org/10.1016/j.polymer.2013.07.035

Graphical abstract:



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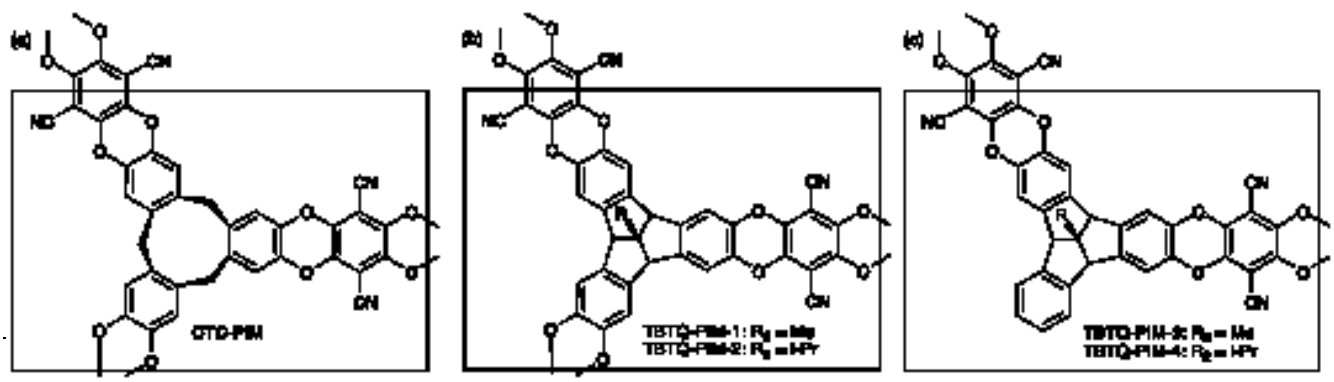
Hydroxyl containing Bowl-shaped "centrotriindane" and propellane-type "triptindane" derivatives, containing peripheral hydroxyl groups, are successful monomers for the preparation of network and non-network polymers of intrinsic microporosity (PIMs).. Nitrogen adsorption measurements reveal apparent BET surface areas in the range of 555–1039 m^2 g^{-1} which can be related to the distinct shape of the monomeric units.

Introduction

Recently, considerable efforts have been made in the synthesis of novel microporous materials which possess high internal surface areas and therefore can have applications in technologies such as hydrogen storage,[3-4] CO_2 capture[5-6] and gas separations.[7-8] Typical examples include metal-organic frameworks (MOFs),[9-10] zeolites[11-12] and activated carbons.[13-14] Increasingly, polymeric microporous materials built from purely organic components such as hypercrosslinked polymer networks,[15-16] covalent-organic-frameworks (COFs)[REF] and polymers of intrinsic microporosity (PIMs) have attracted much interest.[17] Generally, polymers lack microporosity because they have enough conformational and rotational freedom to pack space efficiently. However, PIMs are composed of highly rigid and contorted macromolecules which cannot pack space efficiently, leaving molecular sized interconnected voids.[18] The rigidity is caused by the polymers being composed of fused ring units and the contorted structures arises from the incorporation of non-planar *sites of contortion* such as spiro-centres[19] or triptycene units.[20] PIMs have have attracted interest for applications in hydrogen storage,[2] membrane-based gas separations,[7-8] sensors[21] and heterogeneous catalysis.[22] An attractive feature is that their structure and properties can be tailored by the appropriate choice of monomer precursors. In the past we have shown that concave shaped monomers such as cyclotricatechylene (CTC)[2] or hydroxylated tribenzotriquinacenes (TBTQ)[1] and propeller-shaped triptycenes are suitable structural units for the preparation of PIMs by reaction with 2,3,5,6-tetrafluoroterephthalonitrile (Figure 1).

In order to investigate how further changes in the structure can affect the properties of PIMs, our attention was drawn to the recent work of Kuck and coworkers[25] in which they describe the synthesis of the C_2-symmetrical 2,3,6,7,10,11-hexamethoxy-4b,8b,13,14-tetrahydrodiindeno[1,2-*a*:2',1'-*b*]indene the hydrocarbon core of which was termed "centrotriindane" and the C_{3v}-symmetrical 2,3,6,7,13,14-hexamethoxytriptindane the core of which was called "triptindane". These rigid structural units appeared attractive for the synthesis of novel PIMs. Here we describe the synthesis of both propellane-type "triptindane" and "centrotriindane" monomers **C1, C2** and **C3** containing peripheral hydroxyl substituents, and their subsequent polymerisation with 2,3,5,6-tetrafluoroterephthalonitrile to give the network polymer **POL-A** and the non-network polymers **POL-B** and **POL-C** (Figure 2).

Figure 1. The structures of (a) the TBTQ1 network polymers and (b) the TBTQ non-network polymers.



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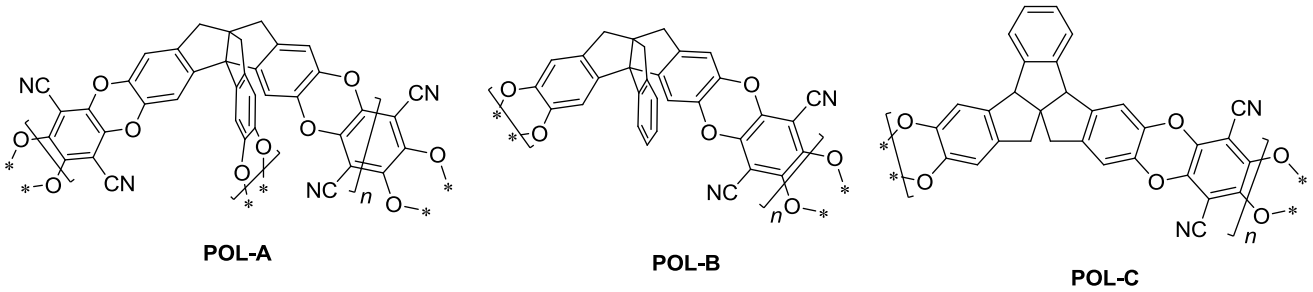

Figure 2. The structure of propellane-type "triptindane" polymers **POL-A** and **POL-B** and the "centrotriindane" ladder polymer **POL-C**.

Experimental

Full experimental details for the multi-step synthesis of, monomers **C1 - C3** and **POL A - C** are given in the supplemental information along with solid state NMR spectra and nitrogen isotherms of the polymers.

Results and discussion

1. Synthesis

The original preparations of 2,3,6,7,10,11-hexamethoxy-4b,8b,13,14-tetrahydrodiindeno[1,2-*a*:2',1'-*b*]indene and 2,3,6,7,13,14-hexamethoxytriptindane reported by Kuck *et al.*[25] were modified to give monomers **C1-C3** suitable for forming network polymer **POL-A** and non-network polymers **POL-B** and **POL-C** (Scheme 2). The key intermediates used for preparing monomers **C1 – C3** are the bisketones **X** and **X**, which could be prepared directly in low yield by a two-fold benzylation of 5,6-dimethoxy-1H-indene-1,3(2H)-dione (**X** R = OMe) or the commercial available 1H-indene-1,3(2H)-dione (**X** R = H), respectively, using 3,4-dimethoxybenzyl bromide . However, better overall yields of bisketones **X** and **X** were obtained using a multi-step synthetic procedure starting with the condensation between veratraldehyde and the diones **X** and **X**, followed by reduction of the resulting benzylidenes and then a single benzylation using 3,4-dimethoxybenzyl chloride. Direct bicyclization of the resulting bis-ketones **8** and **9** with orthophosphoric acid in refluxing toluene gave the hexa- and tetramethoxy-substituted triptindanones **10** and **11** in good yield. Reduction of triptindanones **10** and **11** was achieved by ionic hydrogenation using sodium borohydride in trifluoroacetic acid to form the desired hexa-and tetramethoxy "triptindanes" **12** and **13**. Demethylation of **12** and **13** with BBr_3 was successful and yielded the desired novel monomers **C1** and **C2.**

To gain access to the desired centrotriindane monomers, bis-ketones **8** and **9** were reduced with diisobutylaluminium hydride (DIBAL-H) to give **14** and **15** in quantitative yields (Scheme 2). Cyclization of **14** and **15** were performed readily in Eaton's reagent,[26] to provide a good yield of **16** and **17**. Demethylation of **17** with BBr_3 afforded the target novel monomer **C3**, whereas, demethylation of **16** produced an unstable compound, so, unfortunately, its isolation and its use as a PIM precursor proved impossible.

To assess the structural characteristics of these monomers, crystals suitable for XRD analysis of monomer **C1** and **C3** were grown by slow diffusion of hexane into THF solutions of the monomers. Their solid state molecular structures are shown in Figure 3. Both crystals are clathrates, with THF found as included solvent, a typical feature of catechol-containing molecules[27] (in Figure 3 the included THF is omitted for clarity). It is worth noticing that crystal structures of similar molecules are very rare in the Cambridge Structural Database (CSD). These new monomers appear significantly different from previously reported TBTQ[1] and CTC[2] structures. In fact, in the "triptindane" **C1** (Figure 3 a) the hydroxo groups of the catechol lay in an

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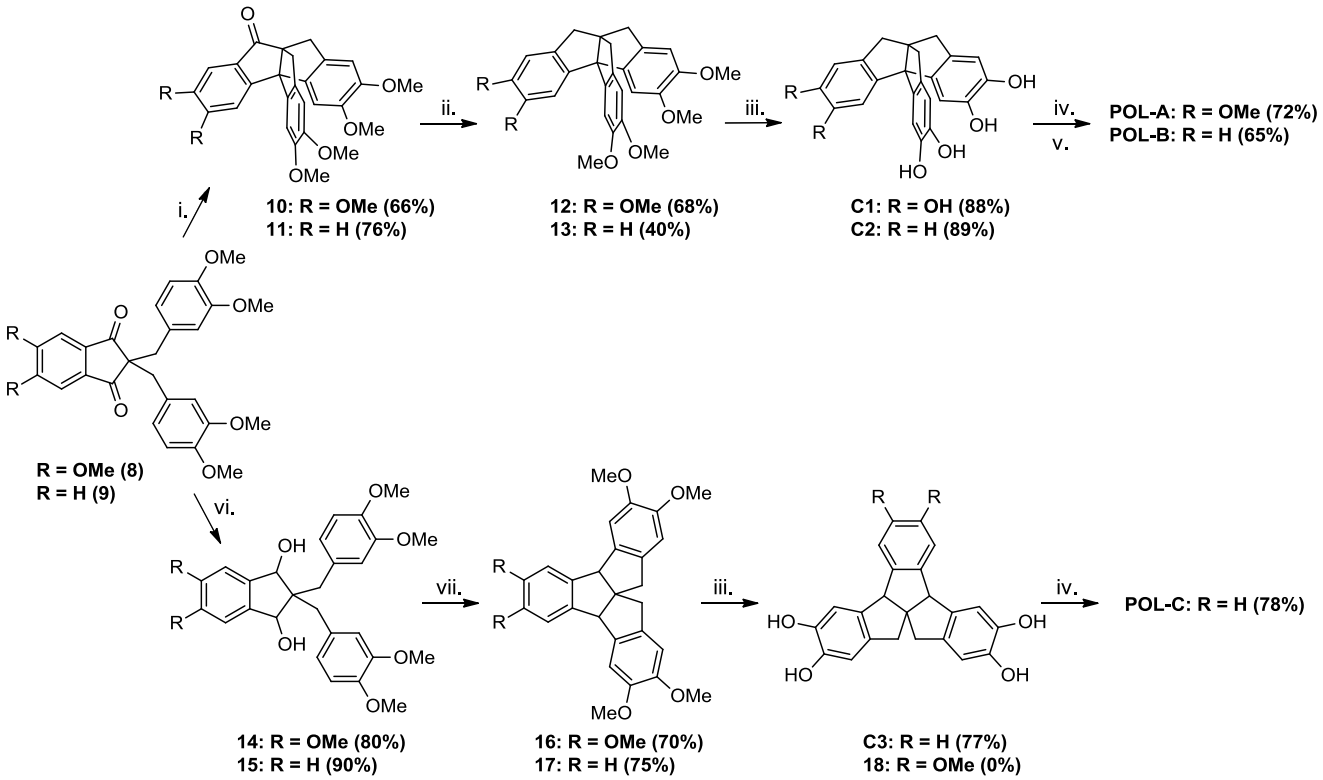

Scheme 2. Reagents and conditions. i. orthophosphoric acid, toluene, 125 ˚C, 16 h. ii. NaBH4, DCM, trifluoroacetic acid, 48 h. iii. BBr3, DCM, 0 ˚C 12–16 h. iv. K2CO3, DMF, 80 ˚C, 16 h. v. K2CO3, DMF, 65 ˚C, 96 h. vi. DIBAL-H, DCM, 4-16 h, 0 ˚C. vii. Eaton's reagent, 2-3 h, RT. iii. BBr3, DCM, 4–12 h, 0 ˚C.

almost perpendicular direction compared to the plane of the "bowl", whereas in the TBTQ (Figure 3 c) they are disposed along the same plane. This will give a completely different polymerization pattern, making the "triptindane" monomer much more similar to a proper triptycene. The "centrotriindane" **C3**, instead, seems representing a sort of compromise between the two (Figure 3 b).

Polymerisation of monomer C**1, C2** and **C3** with the commercially available 2,3,5,6-tetrafluoroterephthalonitrile, by a nucleophilic aromatic substitution reaction commonly used for PIM synthesis, gave **POL-A, POL-B** and **POL-C** (Figure 2). Despite **POL-B** and **POL-C** possessing non-network structures, all three polymers proved to be insoluble in all solvents tested, which precluded characterisation techniques such as Gel Permeation Chromatography (GPC) and solution based NMR. However, characterisation was achieved by use of solid state ^{13}C NMR which gave spectra consistent with the ideal structures of the polymer (see ESI for spectra).

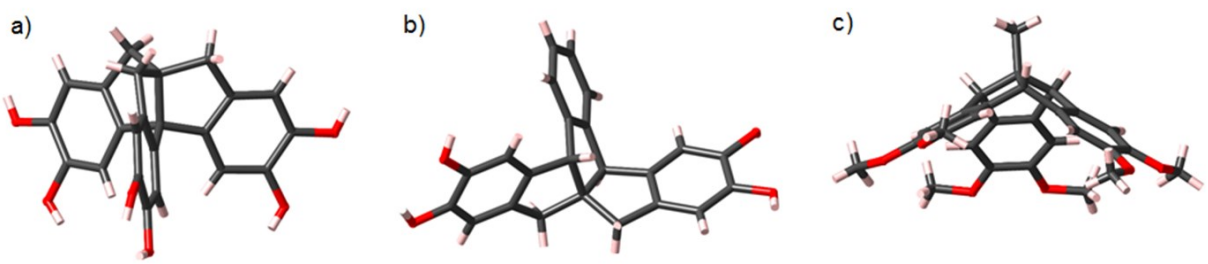

Figure 3. Single crystal XRD data of monomer C1 (a) and C3 (b) and the TBTQ1 (c).

2. Microporosity

Nitrogen adsorption measurements at 77K of powdered samples of POL A - C confirmed their microporosity by demonstrating significant adsorption at low relative pressures (see ESI for isotherms). The apparent BET surface areas and pore volumes of the polymers are shown in Table 1 along with those of the related TBTQ[1] and CTC[2] PIMs. (Trip-PIM??)

Table 1. Summary of polymer properties.

Monomer	Polymer	BET surface area (m^2 g^{-1})	Pore volume (ml g^{-1})[a]
C1	POL-A	1039	0.79
C2	POL-B	653	0.46
C3	POL-C	555	0.43
n/a	CTC-network-PIM 2	830	0.39
n/a	TBTQ-PIM-11	565	0.36
n/a	TBTQ-PIM-21	673	0.41
n/a	TBTQ-PIM-31	511	0.37
n/a	TBTQ-PIM-41	568	0.37

[a]Calculated from amount of nitrogen adsorbed at 77K and relative pressure $P/P_o = 0.98$)

The network polymer **POL-A** which is derived from the "triptindane" structural unit demonstrates greater microporosity than the non-network polymer **POL-B** which is derived from the same structural unit. This is in agreement with previous research[1] which suggests that a network rather than a non-network structure favours porosity. **POL-A** demonstrates also greater microporosity than the CTC-network-PIM[2] and all of the previously reported TBTQ PIMs.[1] This suggests that the "triptindane" structural unit is more rigid than TBTQ and CTC and packs less efficiently, making it more suitable for forming microporous materials. It is notable that the surface area of PIM-triptindane is between that of bowl-shaped PIM-CTC (830 m^2 g^{-1}) and trigonal-planar PIM-trip (1300 m^2 g^{-1}). In addition, it is possible to predict from the crystal structure of **C2** (Figure 3a) that the shape of the developing polymer network more closely resemble that of PIM-trip than PIM-CTC with the monomer promoting the formation of a more regular networked structure during polymerisation.

Conclusions

Novel "centrotriindane" and "triptindane" monomers were successfully synthesised, their structural units were incorporated into polymers and these materials demonstrated microporosity. The network "triptindane" polymer (**POL-A**) had a BET surface area of 1039 m^2 g^{-1}, which was significantly higher than the previously reported CTC-network-PIM [2] and TBTQ PIMs,[1] which suggests that the rigid and contorted "triptindane" structural unit frustrates packing in the solid state and leads to enhanced microporosity relative to CTC and TBTQ. The synthetic route used did allow the formation of tetrahydroxylated monomers useful for the synthesis of non-network polymers (**POL-B** and **POL-C**) which unfortunately proved to be insoluble in all tested solvents. Unfortunately, the hexahydroxylated "centrotriindane" monomer **18** was highly prone to oxidation, making it unsuitable for forming PIMs. The microporosity and solubility of the non-network polymer **POL-C** is comparable to that of the non-network TBTQ polymers which suggests than no benefit is gained from using the "centrotriindane" structural unit.

More recently we have reported the synthesis of a new series of concave shape monomers based on the Four novel TBTQ monomers suitable for forming both network and non-network PIMs were prepared and polymerized They showed apparent BET surface areas ranging from 511 – 673 m^2 g^{-1}. The microporosity of the TBTQ polymers is believed to arise from the highly rigid bowl-shape of their monomer units.[1] Despite their high surface areas, all of the TBTQ polymers failed to match the microporosity of the similarly shaped CTC-network-PIM.[2] This observation was rationalized analysing the single crystal XRD patterns of the respective monomers[23-24] which showed that, in all cases, the TBTQ unit was less concave relative to CTC, as demonstrated by the greater angle between the neighbouring benzene rings.

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Notes and references

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† Electronic supplementary information (ESI) available: Synthetic procedures, physical methodology, nitrogen isotherms and ^{13}C solid state NMR spectra. For ESI see DOI: 10.1039/c0xx00000x

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